

## **Ultra-Thin Composite Membrane-Electrode Assembly For High-Temperature Proton Exchange Membrane Fuel Cells**

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### **Objectives**

- Develop an ultra-thin ( $< 75 \mu\text{m}$ ), durable membrane capable of operation at 100-140°C
- Achieve  $<0.2 \Omega\text{cm}^2$  membrane ohmic resistance and  $<1\%$  crossover
- Attain high ionic conductance with negligible electronic conductivity
- Attain high mechanical strength
- Demonstrate  $>0.6 \text{ V}$  performance at  $400 \text{ mA/cm}^2$  under ambient reformat/air operation at 120°C

### **Technical Barriers**

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- F. Heat Utilization
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- R. Thermal and Water Management

### **Approach**

Develop a solid superacid-Nafion<sup>®</sup> composite membrane electrode assembly (MEA):

- Solid superacids as high-temperature proton conductors and moisture retainers
- Nafion<sup>®</sup> phase as proton conducting binder phase
- Stable support phase added to enhance strength

### **Accomplishments**

- Developed an understanding of MEA performance-controlling factors
- Demonstrated MEA performance of  $\sim 0.6 \text{ V}$  at  $400 \text{ mA/cm}^2$  and membrane ohmic resistance of  $<0.2 \Omega\text{cm}^2$  under system operating conditions [atmospheric, low relative humidity (RH), hydrogen/air stoichs 1.2/2.0] at 120°C

- Achieved  $>750$  mV performance at  $400 \text{ mA/cm}^2$  under 30 psig operating pressure
- Successfully scaled up MEA to  $300 \text{ cm}^2$

### Future Directions

- Understand MEA decay mechanisms in detail
- Further enhance mechanical durability
- Enhance catalyst utilization by further increasing proton conductivity in cathode

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## Introduction

Fuel cells are inherently very efficient and clean, and they offer the best alternative to conventional power generation technologies. For fuel cells to be commercially competitive, issues such as cost, size, and functionality need to be addressed. A desired commercial distributed/stationary fuel cell system is an atmospheric-pressure natural gas-fueled proton exchange membrane fuel cell (PEMFC) system with  $>35\%$  higher heating value (HHV) efficiency,  $>100^\circ\text{C}$  operation for cogeneration, simple construction,  $>40,000$  h reliable life, and  $<\$1000/\text{kW}$  system cost. For the PEMFC to be commercially viable, the performance of critical components, such as the polymer electrolyte membrane in particular, needs to be enhanced. At present, the operating temperature of the state-of-the-art PEMFC is approximately between  $60$  and  $80^\circ\text{C}$ . Carbon monoxide poisoning of the PEMFC anode's precious metal catalyst is a major technical barrier for utilizing hydrocarbon feedstock. Since the poisoning by CO weakens considerably with temperature, one mitigation approach is to operate the PEMFC at higher temperatures. Many other advantages can also be realized, such as faster electrode kinetics, higher quality waste heat for cogeneration, cathode flooding mitigation, and greater ability to remove waste heat.

The baseline Nafion<sup>®</sup> membrane is deficient in terms of ionic conductivity above  $100^\circ\text{C}$  and at low relative humidity (RH), conditions desired for atmospheric-pressure stationary applications. Such conditions tend to dry out the membrane, drastically reducing membrane proton conductivity. Furthermore, the loss of water causes membrane embrittlement, resulting in membrane cracking, reactant cross-leakage and poor electrode-membrane

contact. Therefore, a cost-effective membrane, with proton conductivity that is less sensitive to change in water content, is needed. Another important issue for  $>100^\circ\text{C}$  operation is significantly reduced cell voltage loss. Only a minor portion of cell voltage loss is caused by the membrane ohmic resistance increase. The majority of the voltage loss increase is due to the increase in cathode polarization.

## Approach

The overall objective is to operate a PEMFC at  $100$ - $140^\circ\text{C}$  to improve CO tolerance, mitigate water and thermal management challenges and reduce membrane cost. The basic approach is to develop a composite membrane consisting of mechanical support and high-temperature proton conduction phases. In order to improve cathode performance, incorporating promising solid superacids into the cathode is also pursued.

## Results

A number of ultra-thin composite membranes and MEAs have been developed to improve water retention and proton conduction at  $120^\circ\text{C}$  (Figure 1). Additives/modifiers with specific properties have been synthesized. The performance of the fabricated MEAs in laboratory-scale cells has been characterized to screen promising formulations. About  $0.6$  V performance and  $<0.2 \Omega\text{cm}^2$  resistance at  $120^\circ\text{C}$  and  $400 \text{ mA/cm}^2$  under system operating conditions (atmospheric, low RH, high utilizations) have been achieved (Figure 2). The anode polarization loss is negligible ( $\sim 10$  mV) under these conditions. The MEA Pt loading was  $0.4 \text{ mg/cm}^2$  for each electrode. This represents one of the best cell performances ever reported in the literature under these conditions. Greater than  $750$  mV performance at  $120^\circ\text{C}$  was also

achieved under pressurized operating condition (30 psig) (Figure 3). The promising MEA has been successfully scaled up to nominal 300 cm<sup>2</sup> (Figure 4). The AC-impedance data revealed that the cathode is under mixed ohmic-kinetic control, while mass-transfer loss is minor (Figure 5). Therefore, enhancing proton conductivity in the cathode is expected to further improve cathode performance. This project was completed on June 30, 2003.

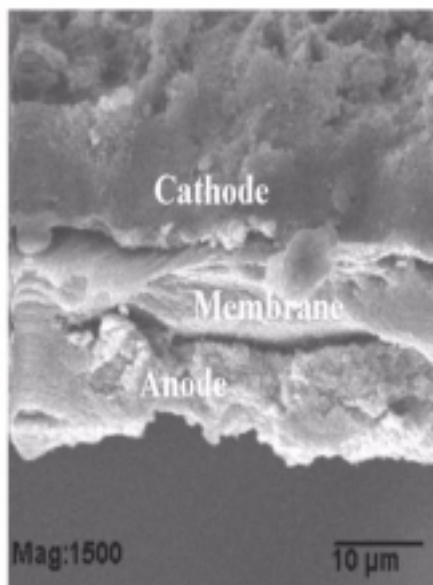


Figure 1. High-performing Ultra-thin MEA (<75 μm)

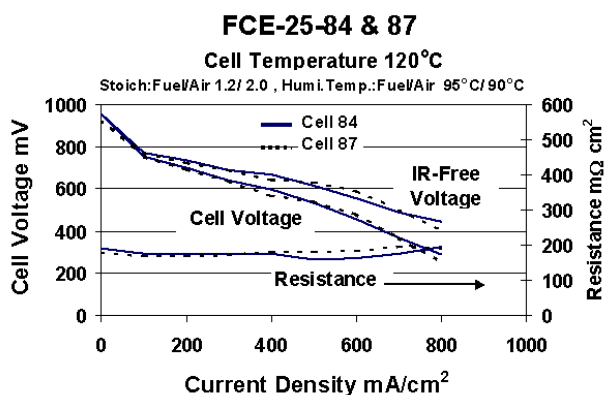


Figure 2. About 0.6 V Performance and <0.2 Ωcm<sup>2</sup> Resistance at 120°C and 400 mA/cm<sup>2</sup> under System Operating Conditions (atmospheric, low R.H., high utilizations) Have Been Achieved

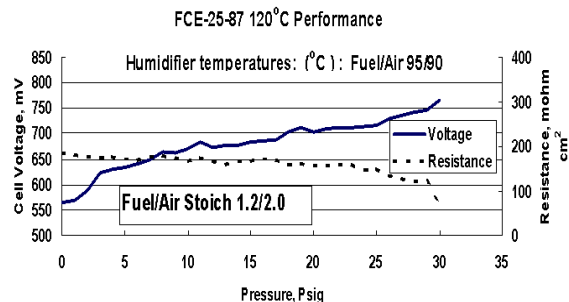


Figure 3. Performance of >0.75 V at 400 mA/cm<sup>2</sup> under Pressurized Operating Conditions Has Been Achieved



Figure 4. Promising MEA Has Been Successfully Scaled Up to 300 cm<sup>2</sup>

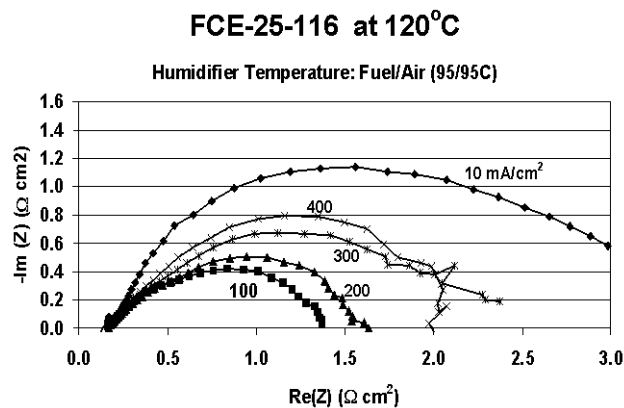


Figure 5. AC-impedance Data Show That the Cathode Is Under Mixed Kinetic-Ohmic Control at 120°C

**Conclusion**

An MEA performance of ~600 mV at 400 mA/cm<sup>2</sup> under system operating conditions has been demonstrated, representing a major milestone towards developing a viable atmospheric PEMFC system. To further enhance cell performance (to a desired 0.8 V at 400 mA/cm<sup>2</sup>), optimization of cathode structure and formulation to enhance proton conduction and cathode catalyst utilization is required.

**FY 2003 Publications/Presentations**

1. Yuh, P. Patel, R. Kopp, and L. Lipp, "Membrane-Electrode Assembly for High-Temperature PEMFC," The American Chemical Society 226th Meeting, New York City, NY, September 7-11, 2003.
2. Yuh, "R&D on an Ultra Thin Composite Membrane for High-Temperature Operation in PEMFC," 2003 Hydrogen and Fuel Cells Merit Review Meeting, Berkeley, CA, May 19-22, 2003.
3. Yuh, "R&D on an Ultra Thin Composite Membrane for High-Temperature Operation in PEMFC," Annual Report to US DOE, for the Period of September 2000 to August 2001.
4. Yuh, "R&D on an Ultra Thin Composite Membrane for High-Temperature Operation in PEMFC," Annual Report to US DOE, for the Period of September 2001 to August 2002.